

PROCESS FOR TRANSPORTING A MULTIPHASE SYSTEM THROUGH A PIPELINE

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The invention relates to a process for transporting a multiphase system, such as for example a gas-petroleum system or a natural gas - condensate system, through a pipeline. The invention also relates to the multiphase system

Said systems are released for example in the production of oil and
10 natural gas at sea, for example on the Continental Shelf of the North Sea. Often the oil contains large quantities of so-called light components. Because the oil is under high pressure in the soil, these components remain in the liquid phase. During the recovery of the oil however these components evaporate as a result of the pressure reduction that occurs. As a result a gas-petroleum system must be transported in the pipelines
15 from the recovery point to the production platform and from the production platform to the coast.

It also occurs that during the recovery of natural gas a condensate is formed of so-called heavy components in the natural gas, for example because before its recovery the gas in the soil has a high temperature and after the recovery cools off
20 or because a condensate is formed due to pressure reduction of the gas (also referred to as "retrograde condensation"). Also in this case a multiphase system is transported then, now in the form of a natural gas - condensate system, from the recovery point to the production platform and from the production platform to the coast.

It is of course also possible that such systems are transported by
25 pipelines overland, for example from a well to a processing plant where gas and liquid are separated.

Said transport operations take place over great distances. Thus, the distance between the well or the recovery point and the platform has increased to dozens of kilometres as a result of the advanced production techniques. The distance
30 between the production platform and the coast can easily increase to a hundred kilometers or even hundreds of kilometers. Therefore the transport of the gas-petroleum and the natural gas - condensate systems is a critical factor in the recovery of petroleum and natural gas. To increase the transport volume a higher pressure drop and/or lines with a larger diameter would have to be used. In both cases much larger
35 investments in the installations are required.

It is the object of the invention to provide a process for increasing the transport volume without the above-mentioned disadvantage.

This aim is achieved in that a multiphase system is transported to which an oil-soluble polymer has been added with a weight-average molecular weight (Mw) of at most 1,500 kg/mol.

The multiphase system preferably comprises an organic liquid. More preferably the multiphase system is a gas-liquid system.

According to a preferred embodiment of the invention Mw is at most 800 kg/mol.

According to a further preferred embodiment of the invention Mw is at most 400 kg/mol.

Preferably Mw is at least 10 kg/mol and more preferably at least 300 kg/mol.

By adding the polymer it becomes possible to transport a larger volume of the multiphase system per unit of time through the pipeline, without it being necessary to increase the pressure drop across the pipeline or to choose a pipeline with a larger transport volume.

The way in which the multiphase system, such as for example the gas-liquid system, is present in the pipeline is for example dependent on the angle of the axis of the line to the horizontal plane and on the flowrates of the gas and the liquid, respectively, in the pipeline. Thus, in a pipeline of which the axis is at a relatively small angle to the horizontal plane, a liquid layer will often be present with on the liquid layer a gas layer, which flow with different velocity through the line.

If there is more liquid in the line and if the gas velocity is high enough waves can be formed that fill the entire pipe diameter. These liquid plugs are called slugs and these slugs give rise to a large loss in pressure during the transport.

Further it is possible that in the multiphase system solids are present, such as for example sand particles. It is also possible that besides the oil or the condensate a liquid aqueous phase or methanol is present.

Examples of suitable polymers to be used in the process according to the invention if an organic multiphase system is used, such as for example natural gas - condensate or gas-petroleum, are oil-soluble polymers. Suitable oil-soluble polymers include for example polysiloxanes, natural rubber, olefin polymers, and polystyrene. The preferred polymers are olefin polymers. Suitable olefin polymers are for example polypropylene, polybutene and copolymers of ethylene and an α olefin

Preferably the selected polymer is easily soluble in the liquid of the multiphase system.

Very good results are achieved if the selected polymer is a (first) olefin polymer containing monomer units of ethylene and at least one alpha olefin and/or if the selected polymer is a (second) olefin polymer containing monomer units of ethylene, at least one alpha olefin and at least one non-conjugated polyene.

The olefin polymers provide a highly improved transport through the pipeline and furthermore offer the advantage that they have a low sensitivity to mechanical degradation (a high "shear stability"), they are chemically inert, they cause no fouling in or blockage of the pipelines and they can easily be added to the multiphase system due to their relatively low viscosity if they are added in a homogeneous solution (compared to ultra high molecular weight polymers).

As monomer units of an alpha olefin the olefin polymers may contain for example monomer units of an alpha olefin of 3-23 carbon atoms. Suitable examples include propylene, 1-butene, 1-pentene, 1-hexene and 1-octene and styrene, monomer units of (alpha, omega) diolefins, such as for example 1,5-hexadiene, 1,6-heptadiene and 1,7-octadiene, branched alpha olefins, such as for example 4-methyl-1-butene, 5-methyl-1-pentene and/or 6-methyl-1-heptene.

More preferably the monomer units of the alpha olefin monomer units are propylene, 1-butene, 1-pentene, 1-hexene and 1-octene. Most preferably the olefin polymer contains monomer units of propylene.

As monomer units of a non-conjugated polyene the (second) olefin polymer contains for example polyene (C), the molecule of which contains a C-C double bond which is polymerisable with for example a Ziegler-Natta catalyst, in addition to at least another C-C double bond and/or polyene (D), the molecule of which contains several C-C double bonds which are polymerisable with a Ziegler-Natta catalyst.

Polyene (C) and polyene (D) can be both aliphatic and alicyclic. Aliphatic polyenes generally contain 3 to 20 carbon atoms.

Suitable examples of polyene (C) include 1,4,8-decatrienes, 1,4-hexadiene and/or 4-methyl-1,4-hexadiene.

Suitable examples of polyene (D) include 1,4-pentadiene, 1,5-hexadiene, 1,7-octadiene and/or 1,4,9-decatriene.

Alicyclic polyenes, with or without a bridge group, may be both mono- and polycyclic.

Suitable examples of alicyclic polyenes (C) include alkylidene norbornenes, in particular the 5-alkylidene-2-norbornenes, in which the alkylidene group contains 1 to 20, and preferably 1 to 8 carbon atoms, and some alkenyl norbornenes, in particular the 5-alkenyl-2-norbornenes, in which the alkenyl group contains 2 to 20 and preferably 2 to 10 carbon atoms and in which the alkenyl group does not contain a terminal double C-C bond, for example 5-(2'-methyl-2' butenyl)-2-norbornene and 5-(3'-methyl-2'butenyl)-2-norbornene.

Preferably polyene (C) is 5-ethylidene-2- norbornene.

Suitable examples of alicyclic polyenes (D) include vinylnorbornene, norbornadiene and the alkyl derivatives, and/or dicyclopentadiene.

Preferably polyene (D) is dicyclopentadiene, 5-vinyl-2-norbornene and/or 1,5-hexadiene is applied.

The (first) olefin polymer contains for example 15-80 mole% monomer units of ethylene and 20-85 mole% of the alpha olefin. Preferably the first olefin polymer contains 35-75 mole% monomer units of ethylene and 25-65 mole% of the alpha olefin, still more preferably the olefin polymer contains 50-70 mole% monomer units of ethylene and 50-30 mole% of the alpha olefin, most preferably the olefin polymer contains 55-65 mole% monomer units of ethylene and 45-35 mole% of the alpha olefin.

Preferably the olefin polymer contains no or only a small quantity of crystallinity, so that an even better solubility in organic liquid systems is achieved.

Preferably the olefin polymer has a crystallinity of at most 5%, measured with the aid of DSC (differential scanning calorimetry). More preferably the polymer has a crystallinity of at most 1%.

The crystallinity is calculated from the heat of crystallisation, derived *per se* from a DSC curve by heating up a polymer sample at a rate of 20°C/min to a temperature of 200°C, keeping it at that temperature for 5 minutes and afterwards recording the curve while the sample is cooled off at a rate of 5°C/min. The crystallinity is calculated from the heat of crystallisation being expressed in J/g with the aid of the formula (I):

$$\% \text{ crystallinity} = \text{heat of crystallisation} / 2.94 \quad (I)$$

According to a further preferred embodiment of the invention the (second) olefin polymer contains 0.1 -10 mole% monomer units of the polyene and the

monomer units of ethylene and the alpha olefin preferably having the molar ratio of the monomer units of ethylene and the alpha olefin of the first olefin polymer. More preferably the (second) olefin polymer contains 0.2 - 8 mole%, more preferably 0.5 - 4 mole%, monomer units of the polyene.

5 It is possible to use conventional polymerisation techniques for the polymerisation of the olefin polymer, such as for example polymerisation in the presence of a Ziegler-Natta catalyst or an anionic catalyst. It is also possible to polymerise in the presence of a metallocene catalyst.

10 The polymerisation may be carried out for example in a solution, in a slurry or in the gas phase.

Preferably the polymerisation is a solution polymerisation. Examples of suitable solvents are linear paraffins with 5 to 8 carbon atoms. Preferably hexane is used as the solvent. It is also possible to use aromatic hydrocarbons as the solvent. Preferably aromatic hydrocarbons are used with only one benzene nucleus, such as for
15 example benzene and toluene. It is also possible to use saturated cyclic hydrocarbons as solvent, preferably having a boiling point that lies in the the boiling point range of the above-mentioned linear paraffins.

If the polymerisation is a slurry polymerisation, preferably liquid propylene is used as the liquid for the slurry.

20 In one preferred embodiment of the invention the olefinic polymer contains polar groups. The polar groups may for example be part of the main chain, may be part of side groups on the chain and/or may be side groups. The presence of these polar groups results in reduced corrosion and in an improved dispersion of small solid particles.

25 Good results are achieved if the polar groups contain at least an oxygen atom and/or a nitrogen atom.

Preferably the olefinic polymer with polar groups is the above-mentioned olefin polymer being grafted with maleic acid, maleic anhydride and/or an ester of maleic acid. Preferably the grafted olefin polymer contains at least 0.01 mole, more preferably at least 0.05 mole, side groups derived from maleic anhydride and/or
30 an ester of maleic acid per 1000 grams of polymer. Preferably the grafted olefin polymer contains at most 0.5 mole side groups derived from maleic anhydride and/or an ester of maleic acid per 1000 grams of polymer.

35 The olefin polymer may be grafted with for example acrylic acid, itaconic anhydride, maleic anhydride, N-vinylpyrrolidone or acrylamide.

Preferably the olefin polymer is grafted with maleic anhydride or the esters of maleic acid with the aid of a free radical initiator, in a solution or in bulk.

Very good results are achieved if grafting is carried out in a solution with for example hexane as the solvent. This reaction is carried out at a temperature in the range of for example 100°C to 250°C and preferably in the range of 120°C to 190°C and still more preferably in the range between of 150°C to 180°C.

Suitable free radical initiators include for example peroxides, hydroperoxides and azo compounds for example azobis-isobutyronitrile, dicumyl peroxide and/or 5-dimethylhex-3-yne-2,5-bis-tertiary-butyl peroxide. The initiator may be used for example in a quantity of 0.005-2 weight % (on the basis of the reaction mixture).

Preferably the grafting is carried out in the absence of oxygen.

If the olefin polymer is grafted in bulk, the maleic anhydride or the maleic acid ester and the free radical initiator is mixed, with a melt of the olefin polymer, for example in an extruder or a mixer. The grafting takes place for example at a temperature between 150°C and 300°C.

The process for grafting the olefin polymer may be carried out both continuously and in a batch process. Preferably however the process for grafting the olefin polymer is carried out in a continuous process. After grafting a subsequent modification, with for example an amine towards an imide, is possible.

The polymers having the molecular weights as mentioned above may also be obtained by mechanical or thermal degradation of higher molecular weight polymers

Good results are achieved if the polymer is added to the multiphase system in a quantity between for example 1 and 1000 ppm. Preferably this quantity is between 5 and 500 ppm and more preferably this quantity is between 10 and 250 ppm.

For the addition to the multiphase system the polymer is preferably dissolved in a solvent suitable for the polymer.

The polymer thus dissolved can be added for example to the multiphase system and mixed with it with the aid of known equipment that is used for adding different additives to multiphase systems, such as for example corrosion inhibitors and additives to counter hydrate formation in petroleum, for example methanol.

Very good results are achieved if as multiphase system, a natural gas -condensate or a gas-petroleum system is transported with the aid of the process

according to the invention. Most preferably the process is applied to a natural gas - condensate system, because a very large reduction in pressuredrop is achieved in that case.

5 The process according to the invention is applied preferably for the transport of a multiphase system in pipelines with a stratified flow, an annular flow or a slug flow. In the case of annular flow a cross-section of the pipe shows that the whole wall is covered with a liquid layer. In the case of stratified flow a cross-section of the pipe shows that part of the wall is covered with a liquid layer.

10 Most preferably the process according to the invention is applied with a stratified flow. → 5027 843

US-A-5107843 discloses the use of a water-soluble drag reducer in a water-oil-gas system. The water-soluble drag reducer is a water-soluble polymer containing polar groups. In contrast the present invention is directed to oil-soluble polymers.

15 EP-A-243127 discloses that a polymer may be added to oil to improve the transport through pipelines. However in contrast to the present invention this process is not concerned with a multiphase system and is directed to a pure liquid system, with consequently completely different transport mechanisms being involved. Further, EP-A-243127 teaches precisely that a polymer with a very high molecular weight must be used, with an intrinsic viscosity of even more than 10 dl/g.

20 SU-A-(11)1361308 discloses that a copolymer of ethylene and propylene with a molecular weight of 56000-60000 can be added to petroleum for transport through pipelines. However in contrast to the present invention this process is not concerned with a multiphase system because it is directed to a heavy petroleum with a high resin content. The polymer is added as a waxinhibitor to counter the formation of aggregates in paraffin-containing resin-like oils. In the multiphase systems that are used in the process according to the present invention it is precisely light oils that are concerned and precisely the problem of improving the transport volume is solved, while in SU-A (11)1361308 the emphasis lies on lowering the pressure which is necessary to restart the oil flow through the pipeline after an incident

30 US-A-3559664 discloses a process for transporting liquid hydrocarbons, with the addition of a block copolymer of ethylene and propylene to the hydrocarbons. However in contrast to the present invention this process is not concerned with a multiphase system because it is directed to a pure liquid system.

35 Further a high-molecular weight polymer is used with an intrinsic viscosity of more than

5 dl/g. These polymers are not shear stable and these polymers cannot be used in conventional pumping systems which are used in the present field of application.

The invention will now be elucidated by means of the following non-restrictive examples.

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Examples I-III and comparative experiments A-C

The polymers used in the Examples I-III are:

- EPM-1: an ethylene propylene copolymer having an ethylene content of 58 mole% grafted with maleic anhydride and capped with N-phenyl para phenylene diamine (NPPDA) and Mw 90,000 g/mol
- EPM-2: an ethylene propylene copolymer having an ethylene content of 58 mole% and Mw of 140,000 g/mol.
- EPM-3: an ethylene propylene copolymer having an ethylene content of 58 mole% and Mw of 90,000 g/mol

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Example I and Comparative Experiment A

In a test rig CO₂ gas to which cyclopentane was added in different ratios was pumped through a pipeline to a storage tank at 25°C at different flowrates. The CO₂ cyclopentane system served as a model for a natural gas - condensate system.

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In Example I, 65 ppm EPM-1 had been dissolved in the cyclopentane whereas in Comparative Experiment A no polymer had been dissolved in the cyclopentane.

A steel pipe with a cross-section of 100 mm was used as pipeline.

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The pressure drop over a section of 5 metres of the line was measured. The temperature amounted to 25°C.

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The results are shown in the Table as a function of the superficial velocity of cyclopentane (v_{sl}) and the superficial velocity of the CO₂ (v_{sg}). Also shown are the pressure drop per metre of pipeline ($\Delta P_{ex. 1}$, in Pa/m) measured in accordance with the example on the multiphase system to which the polymer had been added, and the pressure drop per metre ($\Delta P_{comp. exp.A}$, in Pa/m) measured in accordance with the associated comparative experiment on the corresponding multiphase system without the polymer.

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The effect of the presence of the polymer on the decrease in the pressure drop has been calculated according to the formula (II):

$$\text{Eff \%} = (\Delta P_{\text{comp. exp A}} - \Delta P_{\text{ex. 1}}) / \Delta P_{\text{comp. exp A}} \times 100\% \text{ (II)}$$

Table 1

		Comp. Exp. A	Example I	
Vsl (m/s)	Vsg (m/s)	$\Delta P_{\text{comp. exp A}}$ (Pa/m)	$\Delta P_{\text{ex. 1}}$ (Pa/m)	Eff. (%)
0.06	5.5	27	24	9
0.06	8	52	47	10
0.09	5.5	37	33	9
0.09	8	63	57	11

- 5 Table 1 shows the influence of EPM-1 on pressure drop with CO₂ cyclopentane system. It appears that due to the addition of the polymer (EPM-1) to the multiphase system a relative reduction in pressure drop of up to 11% occurs.

Example II and comparative experiment B

- 10 Example II and Comparative Experiment B were carried out as Example I and Comparative Experiment A, but instead of EPM-1 EPM-2 was used at 50 ppm concentration. The results are given in Table 2.

Table 2

Vsl (m/s)	Vsg (m/s)	Comp. Exp. B	Example II	Eff. (%)
		$\Delta P_{\text{comp. exp A}}$ (Pa/m)	$\Delta P_{\text{ex. 2}}$ (Pa/m)	
0,03	4	9	9	0
0,06	4	13	12	5
0,09	4	18	17	4
0,03	5,5	17	16	4
0,06	5,5	24	20	14
0,09	5,5	33	27	17
0,03	6,7	26	23	12
0,06	6,7	33	27	18
0,09	6,7	45	36	21
0,03	8	38	33	13
0,06	8	49	39	21
0,09	8	55	42	24

Table 2 shows the influence of EPM-2 on pressure drop with CO₂ cyclopentane system. It appears that by the addition of the polymer (EPM-2) to the multiphase system a relative reduction in pressure drop of up to 24% occurs.

Example III and Comparative Experiment C

Example III and Comparative Experiment C were carried out as Example I and Comparative Experiment A, but instead of cyclopentane a light petroleum with a viscosity of 3 centiPoise was used and instead of EPM-1, EPM-3 was used at 50 ppm concentration. The results are given in Table 3.

Table 3

Vsl (m/s)	Vsg (m/s)	Comp. Exp. C	Example III	
		$\Delta P_{\text{comp. exp C}}$ (Pa/m)	$\Delta P_{\text{ex. 3}}$ (Pa/m)	Eff. (%)
0,03	4	23	23	0
0,06	4	27	27	0
0,09	4	33	33	0
0,03	5,5	28	28	0
0,06	5,5	33	32	3
0,09	5,5	38	36	4
0,03	6,7	38	37	4
0,06	6,7	43	40	6
0,09	6,7	49	46	7
0,03	8	48	46	5
0,06	8	54	50	8
0,09	8	59	54	8

Table 3 shows the influence of EPM-3 on pressure drop CO₂ petroleum system. It appears that by the addition of the polymer (EPM-3) to the multiphase system a relative reduction in pressure drop of up to 8% occurs.